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MAGNETIC EXCHANGE IN A CHLORIDE- AND ADENINIUM-BRIDGED LINEAR TRIMER
OF COPPER(II)-OCTACHLOROBIS(ADENINIUM)TRICOPPER(II) TETRAHYDRATE.

by

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ABSTRACT

Magnetic susceptibility measurements on a powdered sample of the linear trimer octachlorobis(adeninium)tricopper(II) have revealed exchange coupling which may be described by the pairwise Hamiltonian $-2J \sum_{i \neq j} \vec{S}_i \cdot \vec{S}_j$. The exchange integral for the coupling between adjacent copper ions is calculated to be -16.1 cm^{-1} when the exchange between terminal ions in the trimer is set equal to zero. The exchange mechanism is described in terms of the orbital pathways which are available and the single ion ground state wave functions.

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INTRODUCTION

In recent years the study of electron spin exchange interactions in magnetically condensed inorganic materials has progressed rapidly. Certainly the greatest effort and success, has been in the study of dimeric complexes, particularly dimeric copper(II) complexes. The theory appropriate for such materials is found to be generally adequate for the description of the magnetic properties. Recently, it has been shown that it is possible to understand the nature and magnitude of the exchange interactions in terms of the chemical and structural features of the molecular system, particularly in the case of hydroxo-bridged copper(II) complexes.^{2,3}

Although the magnetic properties of both dimeric and polymeric copper(II) complexes have been examined extensively, there has been relatively little work on oligomeric copper(II) complexes with more than two copper ions, primarily due to a lack of suitably characterized compounds. Since models of the magnetic behavior of oligomeric compounds must ultimately merge as the number of interesting ions increases from two in the simple dimers to infinity in linear chain compounds, it is desirable to examine linearly interacting systems with intermediate numbers of copper ions.

In the course of our studies of complex formation between adenine and copper(II) chloride in acidic solutions we prepared the known complex octachlorobis(adeninium)tricopper(II) tetrahydrate. The molecular structure (Figure 1) of this material had been determined⁴ by a single-crystal X-ray diffraction study and found to consist of linear trimers of copper ions bridged by both adeninium and chloride ions. These trimers are, in turn, weakly polymerized by chloride bridges to form a linear polymer. Since the inter-trimer interactions are expected to be significantly smaller than the intra-trimer interactions⁵

and to have only negligible effects on the magnetic properties except at very low temperatures, we began an investigation of the magnetic properties of this material. This is to the best of our knowledge, the only complete magnetic investigation which shows the effects of the population of the quartet and doublet states.

EXPERIMENTAL

Preparation: de Meester and Skapski reported⁴ that octachlorobis(adeninium)-tricopper(II) tetrahydrate formed in an attempt to recrystallize dichloro-adeninecopper(II), but they reported no preparative details except to note that the material crystallizes from ca. 2M hydrochloric acid as green elongated prisms. Since several previous attempts to prepare this material in these laboratories were unsuccessful, we report in some detail the routes which do lead to its preparation. a) Preparation in 2M hydrochloric acid. 4.0 g (23.5 mmoles) of copper(II) chloride dihydrate and 1.58g (11.7 mmoles) of adenine (Sigma Chemical Co.) were added to 40 ml of 2M hydrochloric acid. The solution was heated to boiling and maintained at the boiling point until the volume was approximately 25 ml. The solution was cooled to ca. 5°C for two hours, the product isolated by filtration, washed first with 3M HCl and then acetone, and air dried. Yield, 1.9g (2.3 mmoles, 40%) of pale green powder. Anal. Calcd'd for $(C_5N_5H_6)_2Cu_3Cl_8 \cdot 4H_2O$: C, 14.67; H, 2.46; Cu, 23.29. Found: C, 14.83; H, 2.50; Cu, 23.06. Melting point: ca. 125°C darkens to brown, ca. 220° melts with decomposition. b) Alternative Preparations. 1.35 g (10 mmoles) adenine and 2.35 g (14 mmoles) of copper(II) chloride dihydrate were dissolved in 30 ml of water containing 12 mmoles HCl. The solution was boiled until the volume was 15 ml, cooled and filtered giving 0.6g of mustard colored powder (subsequently shown to be $(adenine)CuCl_2$). 30 ml of conc. HCl was added to the filtrate, the solution was heated to boiling and left standing overnight.

Filtration gave 1.3 g of bright green crystals shown to be $(\text{adenineH}_2)\text{CuCl}_4$. The filtrate was boiled to a volume of 15 ml and filtered, giving a small crop of white crystals ($\text{adenine}\cdot\text{HCl}$). This filtrate was boiled to a volume of 8 ml. Filtration gave 0.063 g of pale green crystals. This complex appears to be formed as a persistent contaminant in preparations of other adenine-copper complexes. In particular, what appears to be reasonably clean samples of the compound were formed in low yield in almost all reactions in which copper was in significant excess and the acid concentration was between 2 and 8 M. (In these cases the identity of the material as octachlorobis(adeninium)tricopper(II) tetrahydrate was established by its characteristic melting point behavior rather than by chemical analysis).

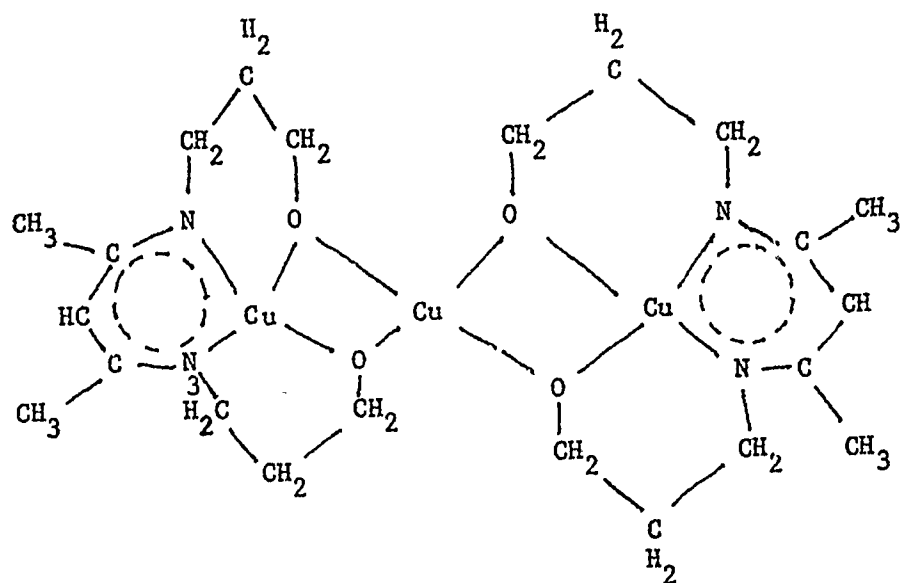
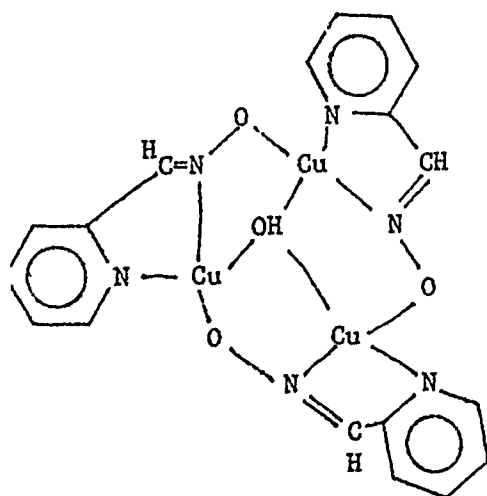
Micro-analyses were by Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

Magnetic Measurements. Magnetic susceptibility measurements were made on a powdered sample of $(\text{C}_5\text{N}_5\text{H}_6)_2\text{Cu}_3\text{Cl}_8\cdot 4\text{H}_2\text{O}$ using a Foner-type vibrating-sample magnetometer⁶ operating at 10 kG as described elsewhere.⁷ Nickel metal was employed as a susceptibility standard. Measurements were made in the temperature range 2 - 160°K. The temperatures were measured with a calibrated GaAs diode. Susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constants⁸ and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} cgsu/Cu atom).

Mull (transmittance) spectra were obtained with a Cary Model 17 recording spectrophotometer using a technique described previously.⁹ Electron paramagnetic resonance (EPR) spectra were recorded with a Varian E-3 spectrometer. Quartz sample tubes were employed for polycrystalline samples. Spectra were calibrated using diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as a field marker. A sample of polycrystalline DPPH taped to a tube containing oxobis(2,4-pentanedionato)-vanadium(IV) in benzene¹⁰ served as a double standard for checking field strength, frequency and sweep rate settings.

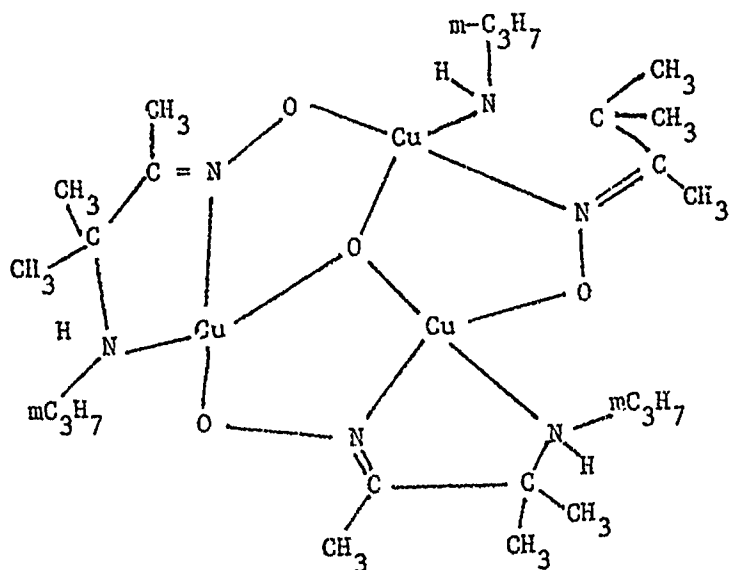
Results and Discussion

There have only been five copper complexes (I-IV) which have been shown unambiguously to be trimeric and which have been thoroughly examined magnetically.¹¹⁻¹⁶ In each of these cases (one strictly linear,¹¹ the others equilateral

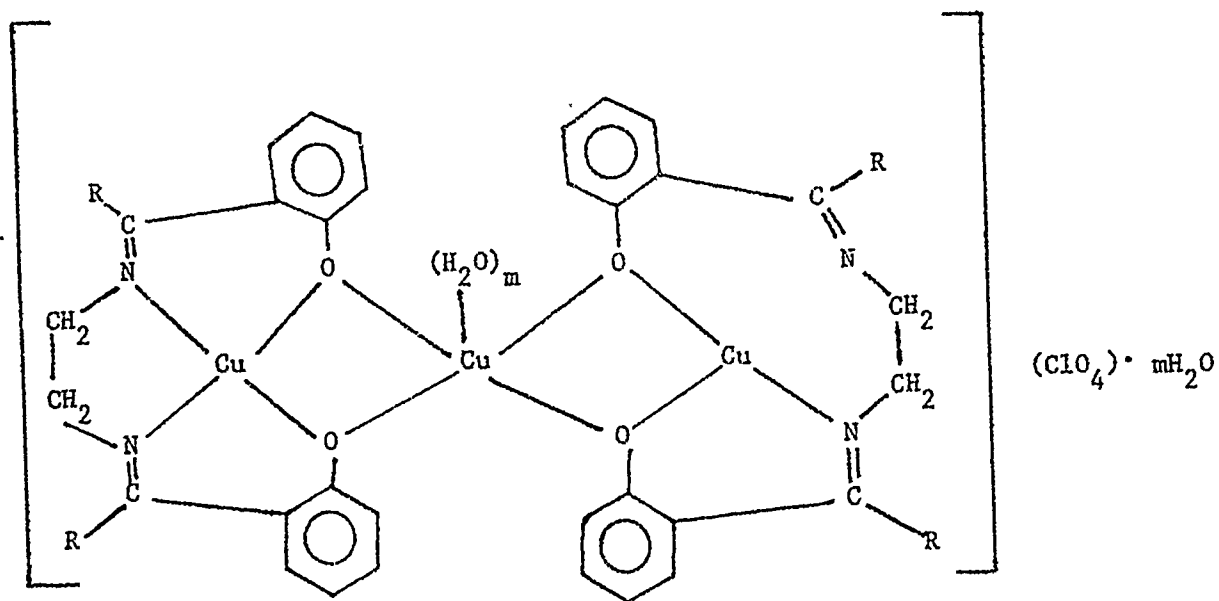
I¹¹

2+

II¹²



III¹³



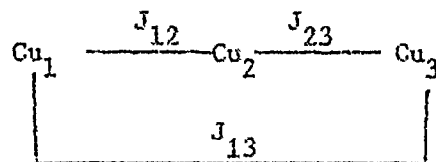
- a) $R = H, m = 2, m = 1$
 b) $R = CH_3, m = 1, m = 0$

IV¹⁴⁻¹⁶

triangular²⁻¹⁶) copper ions are bridged by oxygen ligands and magnetic exchange is fully effective at room temperature, i.e., the complexes have a spin 1/2 ground state and μ_{eff} is independent of temperature. This result implies a value of $|J| > 300 \text{ cm}^{-1}$. Several Schiff base copper(II) trimers have been synthesized and examined magnetically.¹⁵⁻¹⁹ Although crystal structures have not been determined, chemical and physical evidence indicates these Schiff base complexes to be oxygen-bridged trimers. With only one exception these materials exhibit exchange interactions with $J \approx -200 \text{ cm}^{-1}$ and have reduced magnetic moments at room temperature. The magnitude of J in these compounds is comparable to that observed in analogous dimeric Schiff base complexes.² The exceptional case is bis[N,N'-ethylenebis(salicylaldehydato)copper(II)]copper(II) perchlorate trihydrate, (IVa), which is claimed¹⁶ to have $J = -40 \text{ cm}^{-1}$. The crystal structure of the complex "does nothing to aid explanation of the effect".¹⁴ It may well be that the data were improperly processed since there is a disparity in reported room temperature magnetic moments, i.e., $\mu_{\text{eff}} = 1.45^{18}$ and 1.69^{16} B.M. and improper expressions¹⁶ were employed for the magnetic susceptibility.

Dimethylglyoximate and acetylacetonedioximate copper(II) complexes have been examined magnetically²⁰ in the range 100-300°K. Although not established by crystallographic evidence, these materials are believed to have a linear trimeric structure which is in accord with the magnetic data. These complexes differ from those mentioned above in having two-atom (N,O) bridges, and, as expected, the magnitude of the exchange interactions is smaller. Surprisingly, the exchange appears to depend markedly upon the identity of the non-bridging ligands on the terminal copper atoms, changing from $2J = -49 \text{ cm}^{-1}$ when the ligand is water to $2J = -91 \text{ cm}^{-1}$ when it is chloride ion. To date, no trimeric copper(II) complex which exhibits the full range of magnetic behavior possible with intermediate coupling has been examined. Octachlorobis(adeninium)tricopper(II) trihydrate is such a compound and its magnetic behavior is described below.

Magnetic properties of trimeric copper complexes and possible modifications to the theory have been summarized recently.²¹ The theory appropriate for the magnetic properties of trimeric metal complexes has been discussed extensively, originally by Kambe²² and later in more detail²³ for the specific cases of linear trinuclear copper complexes(V) both with ($J_{12} = J_{23} \neq J_{13}$) and without ($J_{12} = J_{23}$;



V

$J_{13} = 0$) end-to-end interaction, as well as for triangular clusters which are equilateral ($J_{12} = J_{23} = J_{13}$) and isosceles ($J_{12} = J_{23} \neq J_{13}$).

The general form of the magnetic data for octachlorobis(adeninium)tricopper(II) trihydrate is appropriate for a trimer with the dominant exchange interactions between adjacent copper atoms. Thus, a plot of reciprocal susceptibility vs. temperature (Figure 2) is linear at high temperature, exhibits a broad shoulder at intermediate temperatures and is again linear at low temperatures. At high temperatures ($T \gg J/k$) the effective magnetic moment $\mu_{\text{eff}}^{160^\circ\text{K}} = 3.05$ B.M. per trimer or $\mu_{\text{eff}}^{160^\circ\text{K}} = 1.76$ B.M. per copper atom ($\mu_{\text{eff}}^{295^\circ\text{K}} = 1.86$ B.M. per copper²⁴), as expected for a system with negligible interactions between trimers. At low temperatures the magnetic moment $\mu_{\text{eff}}^{8^\circ\text{K}} = 1.73$ B.M. per trimer appropriate for a system with a spin 1/2 ground state, i.e., the strong interaction limit.

For a symmetrical linear trimer of copper(II) ions the magnetic susceptibility is given¹⁸ by

$$\chi_m = \frac{N g^2 \beta^2}{4kT} \cdot \frac{\exp(-2J/kT) + \exp(-2J'/kT) + 10 \exp(J/kT)}{\exp(-2J/kT) + \exp(-2J'/kT) + 2 \exp(J/kT)}$$

where J is the exchange integral between the central and terminal copper ion ($J = J_{12} = J_{23}$) and J' the exchange integral between the terminal copper ions ($J' = J_{13}$). The experimental values of $1/\chi$ have been fit to $1/\chi$ calculated using this equation by treating g , J and J' as adjustable parameters and also by holding $J' = 0$ and allowing J and g to vary. The resulting best fit with $J'=0$ is shown as the solid line in Figure 2. The best fit is achieved with $g = 2.14$ and $J = -16.1 \text{ cm}^{-1}$. If J' is allowed to vary, the best fit is achieved with $g = 2.12$, $J = -16.6 \text{ cm}^{-1}$ and $J' = 8.1 \text{ cm}^{-1}$. The ratio of the fitting parameters is 0.94 with the better fit obtaining with the model having the greater number of parameters. For reasons discussed in detail below we believe the fit with $J' = 0$ is more plausible.

The magnitude of J suggests that the dominant pathway for exchange is superexchange through the bridging adenine ligands. The geometry of the chloride bridges in this complex is nearly identical in both Cu-Cl bond lengths and Cu-Cl-Cu bond angles to those observed for the dimeric compounds di- μ -chloro-bis[chloro(dimethylglyoxime)copper(II)]²⁵ and di- μ -chloro-bis[chloro(N,N--dimethylethylenediamine)copper(II)].²⁶ Magnetic susceptibility measurements show that $J = +3 \text{ cm}^{-1}$ in the former complex²⁷ and J is very small and negative in the latter compound.²⁸ By analogy to these systems octachlorobis(adeninium)tricopper(II) tetrahydrate would be expected to exhibit negligible exchange interactions via the chloride bridges.

Compounds in which the bridging atoms are axial with respect to one copper ion and equatorial to the other usually have very small exchange energies. In contrast the adeninium ion bridges equatorial sites on each copper, and superexchange is predicted to be significant.²⁹ In the dimeric complexes [(adenine)₂⁻Cu(H₂O)]₂(ClO₄)₄ and [(adenine⁻)₂Cu(H₂O)]₂ which contains four bridging ligands $2J = -300 \text{ cm}^{-1}$ and -160 cm^{-1} , respectively, via EPR measurements.³⁰ Since the

trimeric complex examined here has only one adenine bridge between each pair of adjacent copper ions, a reasonable estimate of the magnitude of exchange would be $J \sim -20 \text{--} -35 \text{ cm}^{-1}$. This is in at least reasonable accord with the observed value $J = -16 \text{ cm}^{-1}$ and supports the conclusion that exchange occurs via adenine bridges.

The orbital pathways which link the two terminal copper ions are very long, and since the chloride bridges are not expected to transmit significant exchange interactions and since the adeninium bridges are known to transmit antiferromagnetic pairwise interactions, it is difficult to rationalize a sizeable exchange interaction between the terminal coppers.

The EPR spectrum of a polycrystalline sample of octachlorobis(adeninium)tricopper(II) tetrahydrate is shown in Figure 3. The "apparent" g-values are: $g_{||} = 2.060 (\pm 0.005)$ and $g_{\perp} = 2.136 (\pm 0.005)$ with the average g-value $\langle g \rangle = \frac{1}{3}(2g_{\perp} + g_{||}) = 2.11$ being in excellent accord with magnetic susceptibility measurements. The g-values are only apparent since both types of sites within the trimer contribute to the observed spectrum. It is interesting that the EPR spectrum is indicative of the unpaired electrons on the copper ions being in or spending appreciable time in d_z^2 orbitals.³¹ This and the general features of the electronic spectrum (Figure 4) of the compound are readily accounted for in terms of phenomenological crystal field calculations.

The crystal field calculations for the terminal five-coordinate and central six-coordinate copper sites employed the explicit method of Companion and Kourayusky.³² The details of the method have been described elsewhere^{33,34} and need not be repeated here. The θ and ϕ geometrical parameters were taken from the reported structure of octachlorobis(adeninium)tricopper(II) tetrahydrate.⁴ For each of the site calculations a nitrogen atom was placed on the assumed z-axis. The α_4 crystal field parameters were assumed^{33,34} to be: $\alpha_4(\text{nitrogen}) = 10,000 \text{ cm}^{-1}$, $\alpha_4(\text{terminal chloride}) = 5,000 \text{ cm}^{-1}$ and $\alpha_4(\text{bridging chloride}) =$

4,500 cm^{-1} . The calculated "d-d" transition energies for the central copper ion in the terminal are: 7930, 14,210, 14,350 and 15,830 cm^{-1} ; for the terminal copper ions: 6740, 10,570, 11,140, and 12,800 cm^{-1} . These calculated transition energies are in reasonable accord with the observed spectrum (Figure 4). The calculations indicate that transitions below 500 nm are not due to "d-d" excitations. More importantly, the calculations show that the two types of coordination sites in the trimer give rise to ground states having predominately d_z^2 character, a result in full accord with the observed EPR spectrum of the trimer.

As may be seen in Figure 1, the trimers are linked by long copper-chloride bonds (3.274Å) into chains, but it is clear from the magnetic susceptibility data that chain behavior does not obtain. A low-temperature study of the EPR of this material would be very interesting, since it is likely that these interdimer contacts will provide orbital pathways for excited state migration.

ACKNOWLEDGEMENTS

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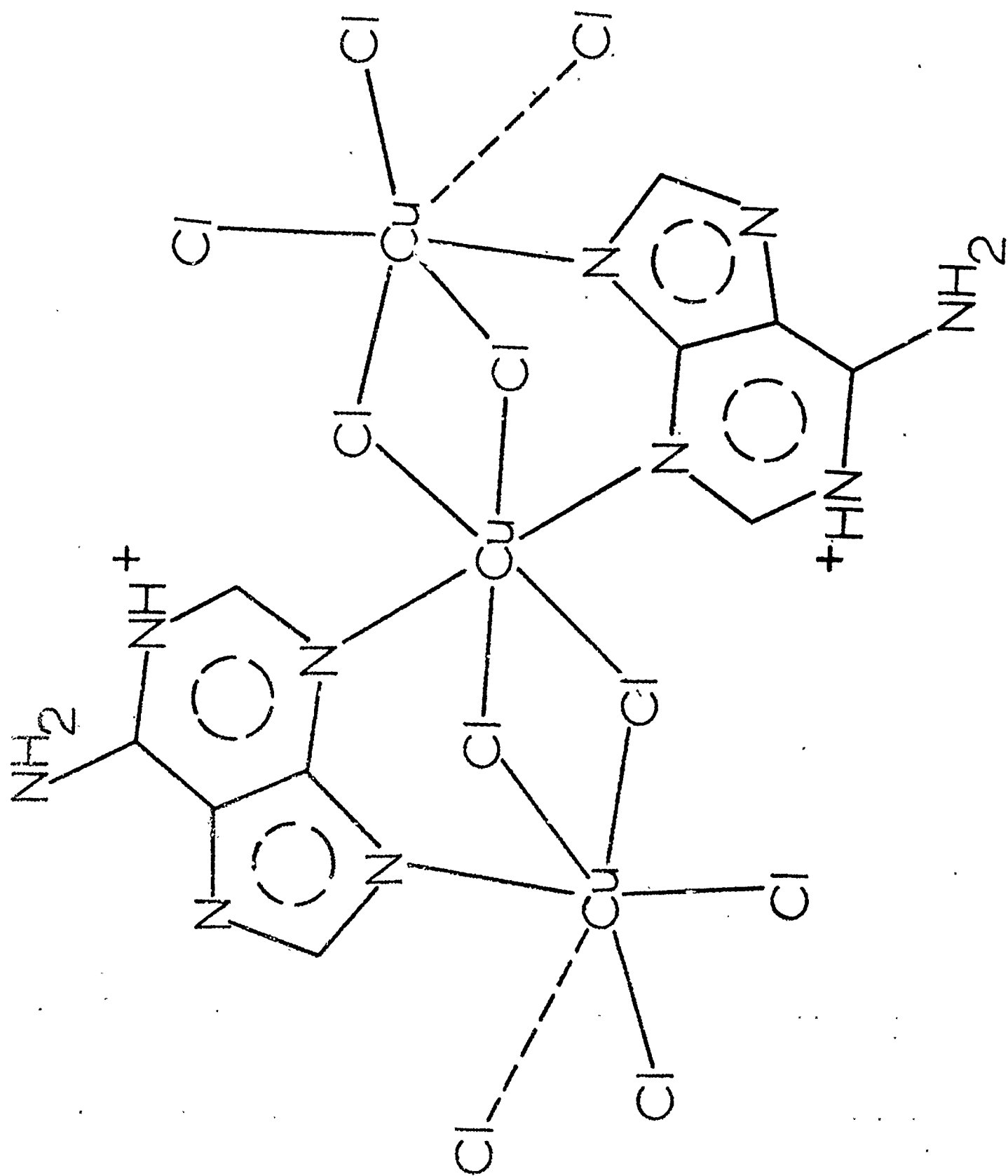
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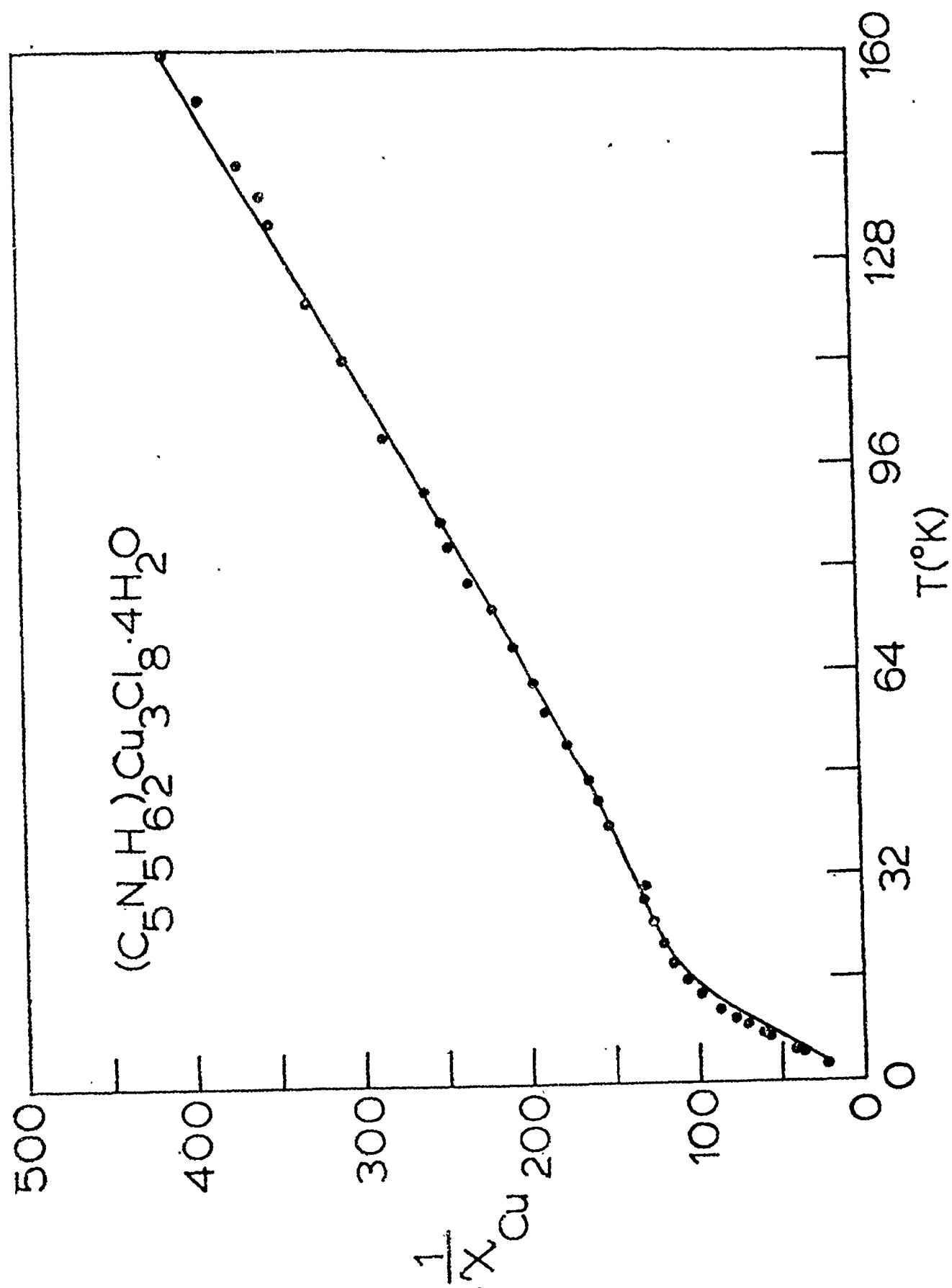
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(b) University of North Carolina, Chapel Hill, North Carolina.
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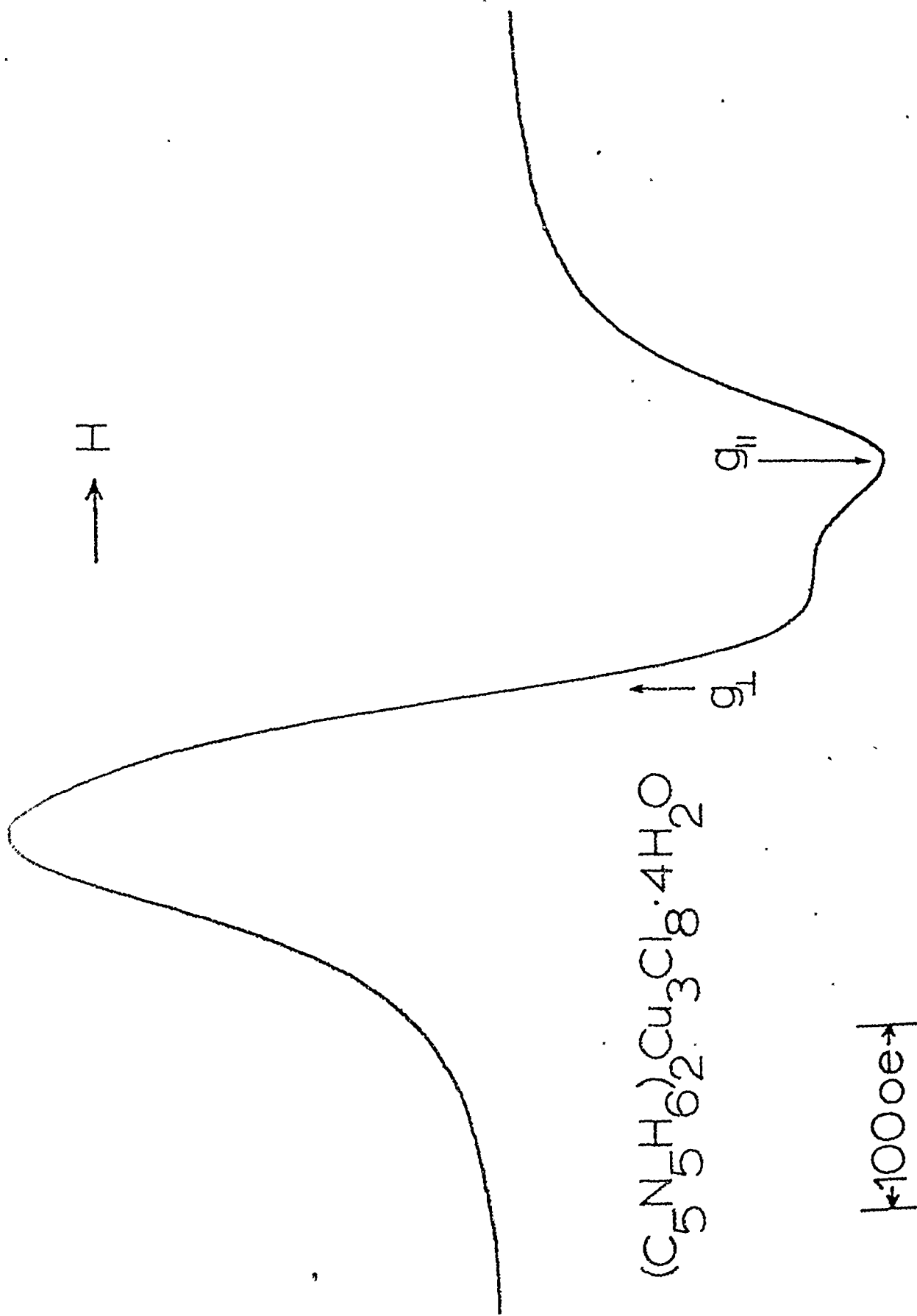
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FIGURE CAPTIONS

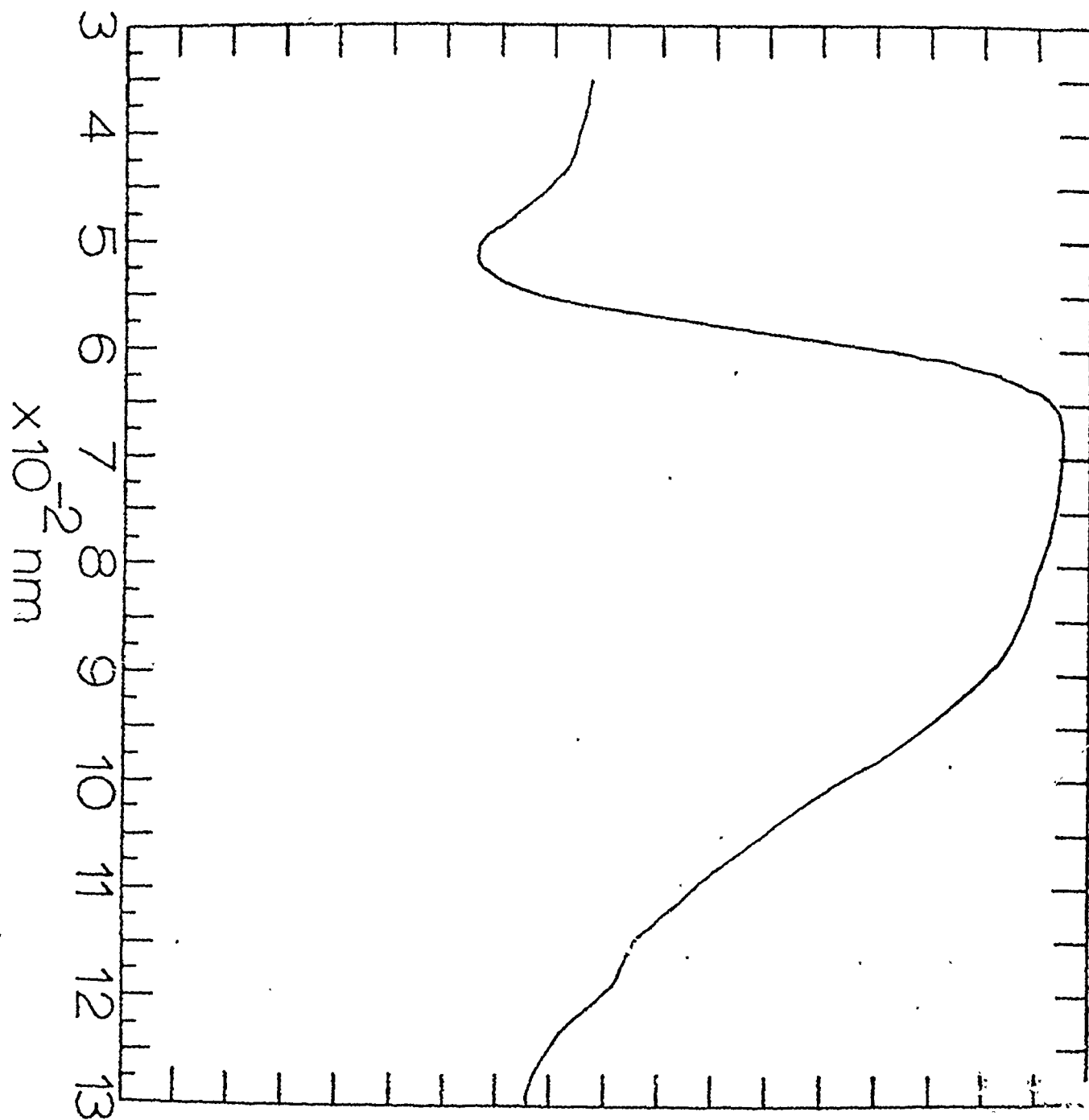
- Figure 1. Structure of octachlorobis(adeninium)tricopper(II) tetrahydrate.⁴
- Figure 2. Reciprocal magnetic susceptibility per copper ion versus temperature for octachlorobis(adeninium)tricopper(II) tetrahydrate.
- Figure 3. Electron paramagnetic resonance spectrum of polycrystalline octachlorobis(adeninium)copper(II) tetrahydrate at room temperature.
- Figure 4. Mull (transmission) electronic spectrum of octachlorobis(adeninium)tricopper(II) tetrahydrate.







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